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(54) Title: BIODEGRADABLE SURFACTANT AND BLENDS THEREOF AS A RINSE AID

(57) Abstract

A surfactant composition comprising: (a) a carrier selected from the group consisting of water, organic solvents, and combinations thereof, the total amount of said carrier being between about 0.01 % and about 30 % by weight based upon the weight of the composition; and (b) an epoxy-capped poly(oxyalkylated) alcohol represented by the formula: $R^3O[CH_2CH(CH_3)O]_x(CH_2CHR^4O)_y[CH_2CH(OH)R^5]_z$ wherein R^3 is a linear, aliphatic hydrocarbon radical having an average of from about 4 to about 18 carbon atoms including mixtures thereof; R^4 is hydrogen or a lower alkyl having between 1 and 6 carbon atoms; and R^5 is a linear, aliphatic hydrocarbon radical having an average of from about 2 to about 14 carbon atoms including mixtures thereof; x is zero or an integer having a value from 1 to about 5; y in an integer having a value from 1 to about 30, and z is an integer having a value of from 1 to about 3.

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BIODEGRADABLE SURFACTANT AND BLENDS THEREOF AS A RINSE AID

The present invention relates generally to a biodegradable surfactant useful in autodish cleaning applications. Another aspect of this invention concerns a liquid surfactant blend that is useful as a rinse aid in industrial and institutional dishwashing applications.

Many of the cleaning compositions heretofore recommended for use in connection with the cleaning of tableware have been subject to one or more significant disadvantages. Perhaps the paramount difficulty involved relates to the tendency of such compositions to leave undesirable spots and films on the washed tableware. As will be recognized, aesthetic considerations rather than purely functional criteria are often of overriding importance in regard to the suitability of a given cleaning composition, especially when contemplated for use in connection with the cleaning of tableware.

Further, environmental concerns have placed a premium on developing surfactants having increased biodegradability. Biodegradability is defined as that property possessed by a material enabling it to be decomposed by bacteria or other living organisms. Ideally, surfactants utilized in the washing of tableware in automatic dishwashers will have a combination of biodegradability characteristics and improved rinsing properties.

The prior art is replete with the disclosure of various surfactant compositions. Illustrative examples include the disclosures contained in U.S. Patent Nos. 3,956,401, 4,207,421, 4,317,940,

4,898,621 and 4,925,587. U. S Patent No. 3,956,401 discloses liquid surfactants having the formula:

$$RO-(CH_2-CH-O)_x-(CH_2-CH_2-O)_y-(CH_2-CH-O)_z-H$$
$$\qquad\qquad\quad |\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\quad R'\qquad\qquad\qquad R''$$

wherein R is a substantially linear hydrocarbon and more particularly an alkyl group having an average of from about 7 to about 10 carbon atoms; R′ is a linear, alkyl hydrocarbon of from about 1 to about 4 carbon atoms; R" is a linear, alkyl hydrocarbon of from about 1 to about 4 carbon atoms; x is an integer of about 1 to about 6; y is an integer of about 4 to about 15; and z is an integer of about 4 to 25.

As another illustration, U.S. Patent No. 4,925,587 discloses hydroxyalkyl polyethylene glycol and hydroxyalkyl polypropylene glycol ether surfactants corresponding to the following general formula:

$$\qquad\quad OH\qquad R^3$$
$$\qquad\quad |\qquad\quad |$$
$$R^1-CH-CH_2-(OCH-CH_2)_n-OR^2$$

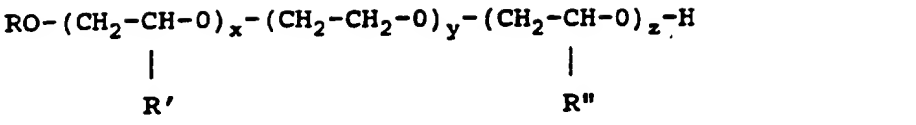
in which

R^1 is a linear C_6-C_{16} alkyl radical;

R^2 is a linear or branched, saturated or unsaturated C_1-C_{22} alkyl radical;

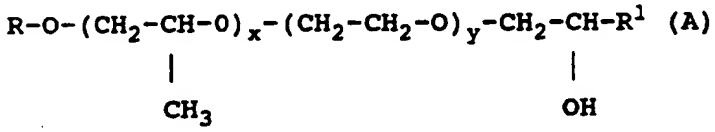
R^3 is hydrogen or a methyl group; and n is a number of from 0 to 30.

As yet another example, U.S. Patent 4,317,940 discloses biodegradable surfactants described as being useful as agricultural emulsifiers and having the following general formula:

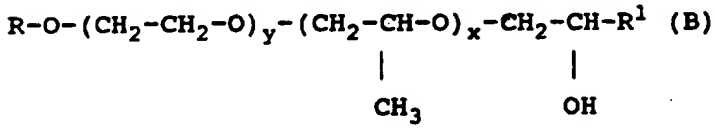


wherein R is a linear, alkyl hydrocarbon chain having an average of from about 6 to about 10 carbon atoms; R′ is a linear, alkyl hydrocarbon of 1 to about 4 carbon atoms; R" is a linear, alkyl hydrocarbon of from about 1 to about 4 carbon atoms; x is an integer of from about 8 to about 12; y is an integer from about 19 to about 25; and z is an integer from about 2 to 7.

As still yet another illustration, U.S. Patent No. 4,827,028 discloses the production of anionic surfactants by reacting an unsaturated dicarboxylic acid such as maleic acid or fumaric acid with at least one epoxy-capped poly(oxyalkylated) alcohol having the formula (A) and (B):



(A)



(B)

wherein R is a hydrocarbon containing radical having from 1 to about 8 carbon atoms; R^1 is a hydrocarbon containing radical having from about 6 to about 18 carbon atoms; x is an integer having a value from about 6 to about 40 and y is an integer having a value from about 8 to about 50. The ratio of x:y is from about 2:8 to about 8:2; and the mole ratio of

dicarboxylic acid to epoxy-capped poly(oxylalkylated) alcohol is from about 1:1 to about 10:1.

The above-described surfactants typically have high caustic solubility, which can be an important surfactant characteristic. Unfortunately, an increased emphasis in the marketplace upon biodegradability characteristics, as well as surfactant cleaning performance in the cleaning of tableware, particularly when utilizing detergent compositions having low phosphate concentrations, has resulted in the adoption by detergent manufacturers of stringent surfactant performance standards for surfactants used in autodish (i.e., industrial and institutional cleaning products). Prior art surfactants do not always meet these stringent performance standards.

As yet another illustration, U.S. Patent 5,294,365 discloses hydroxypolyethers, made by reacting a monoalkyl ether with an alkyl glycidyl ether, for use as low foam surfactants. The compounds of the '365 patent are disclosed therein as being useful in cleaning compositions and rinse aids, especially in automatic dishwashing machines.

Recently, new nonionic surfactants have been discovered which provide an excellent combination of biodegradability, low foaming, and rinsing characteristics, as disclosed in PCT Publication No. WO 94/22800, published October 13, 1994. The surfactant compositions disclosed in the '108 application are epoxy-capped poly(oxyalkylated) alcohols represented by the formula:

$$R^1O[CH_2CH(CH_3)O]_x(CH_2CH_2O)_y[CH_2CH(OH)R^2]_z$$

wherein R^1 is a linear, aliphatic hydrocarbon radical having from about 4 to about 18 carbon atoms including mixtures thereof; and R^2 is a linear, aliphatic hydrocarbon radical having from about 2 to about 26 carbon atoms including mixtures thereof; x is an integer having a value from 1 to about 3; y is an integer having a value from 5 to about 30; and z is an integer having a value of from 1 to about 3.

The surfactants disclosed in the '108 application are said to provide a significant reduction in spotting and filming of tableware, as compared to conventional surfactants, when used in automatic dishwashers. Unfortunately, these surfactants are typically solids, and solids-handling procedures tend to be undesirable and costly from a process engineering standpoint during the preparation of liquid detergents and other hard surface cleaners. Accordingly, new liquid surfactant compositions, in the form of solutions, as well as solid/liquid dispersions, and processes for their preparation, that provide desirable biodegradability and cleaning performance characteristics, together with excellent process ability from a process engineering standpoint, would be highly desired by the cleaning products manufacturing community. The present invention provides one solution to this need.

In one aspect, the present invention relates to a surfactant composition comprising:

(a) a carrier selected from the group consisting of water, organic solvents, and

combinations ther of, the total amount of said carrier being between about 0.01% and about 30% by weight based upon the weight of the composition; and

(b) an epoxy-capped poly(oxyalkylated) alcohol represented by the formula: $R^3O[CH_2CH(CH_3)O]_x(CH_2CHR^4O)_y[CH_2CH(OH)R^5]_z$ wherein R^3 is a linear, aliphatic hydrocarbon radical having an average of from about 4 to about 18 carbon atoms including mixtures thereof; R^4 is hydrogen or a lower alkyl having between 1 and 6 carbon atoms; and R^5 is a linear, aliphatic hydrocarbon radical having an average of from about 2 to about 14 carbon atoms including mixtures thereof; x is zero or an integer having a value from 1 to about 5; y is an integer having a value from 1 to about 30; and z is an integer having a value of from 1 to about 3.

In another aspect the present invention relates to a surfactant composition comprising a liquid blend of components (a) and (b), each of said components being epoxy-capped poly(oxyalkylated) alcohols represented by the formulae:

(a) $R^1O[CH_2CH(CH_3)O]_p(CH_2CH_2O)_q[CH_2CH(OH)R^2]_r$ wherein R^1 is a linear, aliphatic hydrocarbon radical having an average of from 4 to 12 carbon atoms including mixtures thereof; and R^2 is a linear, aliphatic hydrocarbon radical having an average of from about 2 to about 4 carbon atoms including mixtures thereof; p is an

integ r having a value fr m 1 to about 5; q is an integer having a value from 1 to about 30; and r is an integer having a value of from 1 to about 3; and,

(b) $R^3O[CH_2CH(CH_3)O]_x(CH_2CH_2O)_y[CH_2CH(OH)R^4]_z$ wherein R^3 is a linear, aliphatic hydrocarbon radical having an average of from about 4 to about 18 carbon atoms including mixtures thereof; and R^4 is a linear, aliphatic hydrocarbon radical having an average of from about 2 to about 14 carbon atoms including mixtures thereof; x is an integer having a value from 1 to about 5; y is an integer having a value from 1 to about 30; and z is an integer having a value of from 1 to about 3, the weight ratio of component (a) to component (b) being within the range of between about 1:10 and about 10:1, with the proviso that amount of component (a) is sufficient to maintain said blend as a liquid.

In yet another aspect, the present invention relates to a liquid automatic dishwasher composition comprising either the above-described surfactant composition or the above-described liquid blend and additionally comprising at least one component selected from the group consisting of detergent builder, bleach, anti-wear agent, and mixtures thereof.

In yet another aspect, the present invention relates to a cleaning composition for cleaning hard surfaces comprising an aqueous or organic solvent and the above-described surfactant composition or

liquid blend of epoxy-capped poly(oxyalkylated) alcohols as a surfactant.

In still another aspect, the present invention relates to a surfactant composition comprising a liquid or solid carrier and a compound of the formula:

$$R^6O[CH_2CH(CH_3)O]_d(CH_2CH_2O)_e[CH_2CH(OH)(CH_2)_3CH_3]_f$$

wherein R^6 is a moiety selected from the group consisting of butyl, hexyl, octyl and decyl, and combinations thereof, d is an integer between 1 and 3 (preferably 1), e integer between 9 and 11 (preferably 10), and f is an integer between 1 and 3 (preferably 1).

These and other aspects will become apparent upon reading the following detailed description of the invention.

The surfactant composition of the present invention suitably comprises a surfactant and a carrier or a surfactant blend. The composition is suitably employed in the form of a solution, emulsion or dispersion of the surfactant or surfactant blend. Preferably, the blend is in the form of a solution without the need for a carrier.

The basic components of the blend of the present invention are at least two surfactants comprising (and advantageously consisting essentially of) four components, namely a linear alcohol, propylene oxide, ethylene oxide, and an epoxy cap. For each of the surfactants in the blend, the epoxy cap and the linear alcohol serve as a hydrophobic, oil-soluble portion of the molecule. The ethylene oxide groups form the hydrophilic, water-soluble elements of the molecule.

It has now been surprisingly discovered by the present inventors in accordance with one aspect of the present invention that a particular surfactant composition, as identified in Example 5 hereinbelow, exhibits an unexpectedly high egg soil defoaming efficacy in accordance with standard test protocol CSMA Method DCC-01, as well as a very low foam generating capacity as measured by the Ross Miles Foam Height Test regimen. In addition, this product possesses excellent biodegradability, as well as rinse properties as defined by CSMA Method DCC-05A, Glassware Deposition Rinse Test. This combination of properties make it ideal for use as an automatic dishwashing detergent/rinse aid.

It has also been surprisingly discovered in accordance with another aspect of the present invention that liquid blends of surfactants within the scope of the present invention provide significant advantages, relative to presently-available commercial surfactants, based upon the performance characteristics of the liquid blends in cleaning tableware, the rinsing characteristics, and the biodegradability of the blends. Without wishing to be bound by any particular theory, the present inventors believe the liquid nature of the blends is achieved by virtue of the requirement that the blend contain at least some amount of a surfactant having no more than six (6) carbons contained in the epoxide portion of the molecule. In addition, the biodegradability and performance characteristics of the blend are believed to be at least partly attributable to the ordered structure of the compositions in which limited numbers of propylene

oxid groups are directly attached to the alcohol followed by the addition of the ethylene oxide groups and capping using an 1,2-epoxyalkane. While maintaining this ordered structure, it is desired to also have low ratios of propylene oxide groups to ethylene oxide groups. For example, preferred ratios of propylene oxide groups to ethylene oxide groups are in the range of about 1:5 to about 1:30, and more preferably from about 1:10 to about 1:20.

Generally, each of the poly(oxyalkylated) alcohols in the blend are suitably produced by condensing an aliphatic alcohol, or mixture of alcohols, having an average chain length of from 4 to about 18 carbon atoms, preferably from about 4 to about 12, and more preferably from about 6 to about 10 carbon atoms, initially with propylene oxide followed by capping this condensation product with ethylene oxide. The methods used for condensing and capping may be any of the well-known methods described in the art. Preferably, these reactions occur at elevated temperatures in the range of about 120°C to about 180°C, and more preferably at from about 140°C-160°C. It is also preferred to carry out such reactions in the presence of an effective amount (e.g. about 0.005% to 1% by weight of the alcohol) of a suitable alkaline catalyst(s) such as a catalyst selected from the group of hydroxides of alkali metals, alkaline earth metals, alkali metal alcoholates, boron trifluoride (BF_3), and combinations thereof. The preferred catalyst is potassium hydroxide (KOH).

Epoxy compounds useful for making the epoxy-capped poly(oxyalkylated) alcohols of the

present invention include any 1,2-epoxyalkanes, or mixtures thereof, having a hydrocarbon chain containing an average of about 2 to about 26 carbon atoms, with the proviso that at least one of the surfactants in the blend (namely the component (a) surfactant described above) contain between two and four carbons on this hydrocarbon chain. Preferably, the 1,2-epoxyalkane has a linear, aliphatic hydrocarbon chain containing an average of from about 8 to about 20 carbon atoms, and more preferably an average of from about 10 to about 16 carbon atoms. Generally, 2 to 4 carbons is preferred if a high cloud point composition is desired, 6 to 10 carbons is preferred to optimize defoaming efficacy, and 12 to 22 carbons is desired to optimize rinsing efficacy. Various 1,2-epoxyalkane compounds are commercially available from Atochem North America Inc., Philadelphia, PA under the product names VIKALOX 11-14, VIKALOX 12, VIKALOX 16 and others.

The novel surfactant compositions of the present invention provide improved surface treatment of the tableware by the rinse water and subsequently reduces spotting and filming. These epoxy-capped poly(oxyalkylated) alcohols can be formulated in powder and liquid detergent products for automatic dishwashers or in hard surface cleaning products, such as bathroom tile, using methods commercially practiced in the detergent industry. These formulations can include, for example, detergent builders, chelating agents, bleaches, anti-wear agents, and combinations thereof, among others.

Suitable detergent builders include inorganic builders such as sodium tripolyphosphate (STPP), sodium carbonate, zeolites and mixtures thereof. Where STPP is the detergent builder, the STPP may be employed in the compositions in a range of about 8 to 35 wt.%, preferably about 20 to 30 wt%, and should preferably be free of heavy metal which tends to decompose or inactivate the preferred sodium hypochlorite and other chlorine bleach compounds. The STPP may be anhydrous or hydrated, including the stable hexahydrate with a degree of hydration of 6 corresponding to about 18% by weight of water or more.

Organic builders can also be used including nitrilotriacetic acid and alkali metal salts of tartaric or citric acid.

Where used, a chelating agent can be any one of a wide range of organic or inorganic sequestering agents, examples including phosphoric acid, amino polycarboxylic acids such as ethylene diamine tetraacetic acid (EDTA), NTA and DETPA, and polycarboxylic acids such as lactic acid, citric acid, tartaric acid, gluconic acid, glucoheptonic acid, mucic acid, galactonic acid, saccharic acid, fumaric acid, succinic acid, glutaric acid, adipic acid and their alkali metal or ammonium salts. Citric or tartaric acid are preferred chelating acids. The chelating agent if included is present in an amount of up to about 30% and normally lies in the range from about 5% to about 20% by weight. Highly preferred compositions use from about 5% to about 10% by weight of chelating agent in order to

minimize any attack by th chelating agent on the glass.

When a bleach is a component in the formulation, the bleach may be an organic chlorine containing bleach, for example, trichloroisocyanuric acid, dichloroisocyanuric acid or a salt of dichloroisocyanuric acid. Preferably a sodium or potassium salt such as trichloroisocyanuric acid and is employed in an amount of, for example, 1 to 5% and more preferably 2 to 3% by weight in the cleaning composition. Inorganic bleaching compounds such as chlorinated trisodium polyphosphate (TSPP) or lithium hypochlorite may also be used.

The dishwasher formulations may also include anti-wear or anti-corrosion agents such as an alkali metal silicate, preferably sodium silicate, and may be present in a ratio of 0.1 to 3 and preferably 0.2 to 1 mole per mole of alkali in the cleaning composition.

Alkalinity may be provided by an alkali metal compound, for example, sodium or potassium hydroxide and/or carbonate.

Further suitable conventional ingredients for inclusion in the compositions are hydrotropic agents such as xylene sulfonates, alcohols, perfumes and coloring agents.

The present invention as described herein provides liquid blends useful as nonionic surfactant/rinse aids and characterized by excellent cleaning efficacy and biodegradability. These products are suitable for use in both industrial and institutional and automatic dishwashing applications, since the liquid blends provide an

exc llent combination of low foaming, excellent rinsing, and efficient removal of high protein soil. These results are particularly surprising since, in general, prior art linear alcohol alkoxylates capped with 1,2-epoxyalkanes which are efficacious with regards to defoaming in high protein soils are either relatively insoluble in water, thus forming cloudy dispersions, or possess relatively poor rinsing properties. In turn, prior art linear alcohol alkoxylate products which are highly water soluble tend to have poor defoaming characteristics in high protein soil. In contrast, select mixtures of capped linear alcohol alkoxylates made in accordance with the present invention provide a product with both excellent rinsing properties and highly efficacious defoaming properties, especially with regard to various high protein soils.

The formulation of the product blends with desirable properties in accordance with the present invention was determined based upon statistical experimental design techniques involving individual compositions of a wide range of molecular structure. This insured the potential for providing blends over a reasonable range of cloud points and possessing the desirable properties of excellent machine defoaming, rinsing efficacy, and solution stability. Although binary mixtures were prepared in the working examples provided hereinbelow, terinary or quaternary mixtures are suitably employed, if desired, within the scope of the present invention.

As demonstrated by the working examples provided hereinbelow, liquid blend products of the present invention are suitably formulated to meet

were then formulated to meet the performance requirements for industrial and institutional (so-called "I&I") surfactants, as well as the performance requirements for automatic dishwashing surfactants and rinse aids.

The following examples are intended to illustrate, but in no way limit the scope of, the present invention. All parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

Preparation of a Liquid Blend of this Invention

Part A- Preparation of a Solid Surfactant

To a 1000 ml round bottom 3-necked flask fitted with a thermometer (with a Therm-O-Watch controller), a magnetic stirrer, a 250 ml equilibrated dropping funnel (itself fitted with a nitrogen inlet), and a nitrogen outlet was added 500 grams (0.597 moles) of an alcohol alkoxylate precursor containing 1 mole of Alfol-610 (Vista Chemical), 1 mole of propylene oxide and 15 moles of ethylene oxide added in the order described. To this vessel was added 2.0 grams (0.035 moles) of potassium hydroxide as a catalyst. The reaction vessel was supplied with a heating mantle and the temperature was brought to 120±3°C. The temperature was maintained at 120±3°C for 1½ hours. The temperature was then raised to 155°C. At the end of this time 93.13 grams (0.597 moles) of 1,2-epoxydecane (Atochem) was added through the dropping funnel. The addition took place over less than 10

minutes. Th reaction mixture was post-reacted at 155±3°C for 4½ hours. At the end of this time the product was cooled and removed from the flask. The cloud point of a one percent solution of the product in water was 3°C. The hydroxyl number was 55.4 and the % primary hydroxyl was 17.7%.

Part B- Preparation of a Liquid Surfactant

To a 1000 ml round bottom 3-necked flask fitted with a thermometer (with a Therm-O-Watch controller), a magnetic stirrer, a dry ice/acetone condenser, a 100 ml equilibrated dropping funnel (itself fitted with a nitrogen inlet), and a nitrogen outlet was added 500 grams (0.597 moles) of an alcohol alkoxylate precursor containing 1 mole of Alfol-610 (Vista Chemical), 1 moles of propylene oxide and 15 moles of ethylene oxide added in the order described. To this vessel was added 2.0 grams (0.035 moles) of potassium hydroxide as a catalyst. The reaction vessel was supplied with a heating mantle and the temperature was brought to 120±3°C. The temperature was maintained at 120±3°C for 1½ hours. The temperature was then raised to 155°C. At the end of this time 42.98 grams (0.597 moles) of 1,2-epoxybutane (Dow Chemical) was added through the dropping funnel. The addition took place over approximately 1 hour. A slow rate of gentle reflux of the butyleneoxide was maintained. The reaction mixture was post-reacted at 155±3°C for 4½ hours. At the end of this time the product was cooled and removed from the flask. The cloud point of a one percent solution of the product in water was 72°C.

The hydroxyl number was 58.6 and th % primary hydroxyl was 16.1%.

Part C- Blending of the Surfactants from Part A and Part B

Preparation of a Liquid Blend

To 70 grams of the product described in Example 1 was added 30 grams of the product described in Example 2. The cloud point of a one percent solution of the product in water was 28°C.

EXAMPLE 2

Preparation of an Aqueous Solution of the Liquid Blend of Example 1

To 80 grams of the product described in Example 1, Part C, was added 20 grams of water, and the resulting product was a clear, aqueous liquid.

EXAMPLE 3

Preparation of Another Liquid Blend

To 50 grams of the product described in Example 1, Part A, was added 50 grams of the product described in Example 1, Part B. The cloud point of a one percent solution of the product in water was 42°C.

EXAMPLE 4

To 20 grams of the product described in Example 3 was added 80 grams of water.

An Automatic Dishwasher Foam Test (CSMA DCC-01) and Glassware Deposition Rinse Test (CSMA DCC-05A) were used to evaluate products of this invention. Comparisons were made against CASCADE cleaner, a commercial automatic dishwashing product of Procter & Gamble, and against POLY-TERGENT SLF-18 cleaner, a proprietary Olin product, in an evaluation for both rinse and defoaming properties.

AUTOMATIC DISHWASHER EVALUATION

Foaming Test

Measurements are made of the ratio of revolutions of the dishwasher rotor with detergent and soil as a percentage of the revolutions in water alone. Milk and egg soils are employed in this test. The higher the ratio, the more efficient is the detergent.

Table 1- Comparison of Cleaning- Ratio (%)		
	Milk Soil	Egg Soil
Product of Example 1	100	100
CASCADE cleaner	91	94
POLY-TERGENT SLF-18	100	98

Glassware Rinse Test

Glassware was evaluated for spotting, streaking and filming on a scale of 1 to 5, where 1 shows no spots, streaks or film and 5 indicates a glass completely covered with spots, streaks and film.

Table 2- Rinse Test	Spotting	Streaking	Filming	Sum
Product of Example 1	4.1	1.0	2.6	7.7
Cascade	3.2	1.0	3.3	7.5
SLF-18	3.5	1.0	3.4	7.9

INDUSTRIAL & INSTITUTIONAL (I&I) DISHWASHER EVALUATION:

An I&I procedure for the evaluation of glassware rinsing efficacy was developed. This methodology is a variation of the autodish procedure described in CSMA DCC-05A. The measurement of the glassware with regards to spotting, streaking and filming was identical to that in the procedure described above in IV. Rinse aids were evaluated as 20% solutions in water at a 100 ppm use level in the

I&I machine. Comparisons were made to commercial products at identical use levels.

Table 3- Rinse Test	Spotting	Streaking	Filming	Sum
Product of Example 2	1.3	1.7	1.9	4.9
Product of Example 4	1.4	2.7	2.1	6.2
QUICK & DRY	1.3	2.1	2.1	5.5

EXAMPLE 5

Preparation and Testing of a Preferred Surfactant Composition Having the Structural Formula:

$R^3O[CH_2CH(CH_3)O](CH_2CH_2O)_{10}[CH_2CH(OH)(CH_2)CH_3]$ wherein R^3 is a mixture of butyl, hexyl, octyl and decyl.

Preparation Procedure:

To a 500 ml round bottom 3-necked flask fitted with a thermometer (with a ThermoWatch controller), a magnetic stirrer, a 50 ml equilibrated dropping funnel (itself fitted with a nitrogen inlet), and a nitrogen outlet was added 100 grams (0.162 moles) of an alcohol alkoxylate precursor containing 1 mole of Alfol-610 (Vista Chemical), 1 mole of propyleneoxide, and 10 moles of ethyleneoxide added in the order described. To this vessel was added 0.3 grams (0.0054 moles) of potassium hydroxide as catalyst. The reaction vessel was supplied with a heating mantle and the temperature was raised to 120 ± 3°C and maintained at that temperature for 1½ hours. At the end of this time 16.44 grams (0.162 moles) of 1,2-epoxyhexane (Aldrich Chemical, 97%)

was added dropwise over 20 minutes. The reaction mixture was then post reacted at 150 ± 3°C for 4½ hours. At the end of this time the product was cooled to room temperature and removed from the flask. The cloud point of a one percent solution of the product in water was 23°C. The hydroxyl number was found to be 76.7 and the percent primary alcohol was 11.7%.

DISHWASHER EVALUATION

An Automatic Dishwashing Foam Test (CSMA DCC-01) and Glassware Deposition Rinse Test (CSMA DCC-05A) were used to evaluate the product of this invention. Comparisons were made to SLF-18, a proprietary Olin Product, Cascade, a commercial dishwashing detergent (Procter and Gamble), and to a "biodegradable" auto-dish product as described in U.S. Patent No. 4,925,587 (Henkel).

Foaming Test

Measurements are made of the ratio of the revolutions of the dishwasher rotor with detergent and soil as a percentage of the revolutions in water alone. Milk and egg soils are employed in this test. The higher the ratio, the more efficient is the detergent.

Table 4- Cleaning	Milk Soil	Egg Soil
Product of Example 5	100	100
SLF-18	100	98
Cascade	100	94
Product of U.S. Patent No. 4,925,587	100	70

Glassware Rinse Test

Glassware was evaluated for spotting, streaking and filming on a scale of 1 to 5 where 1 shows no spots, streaks or film and 5 indicates complete covering of the item with spots, streaks or film. This methodology uses an exponential scale, not a linear one.

Table 5- Rinse Test	Spotting	Streaking	Filming	"Sum"
Product of Example 5	2.3	1.0	1.4	4.7
SLF-18	3.5	1.0	3.4	7.9
Cascade	3.2	1.0	3.3	7.5
Product of U.S. Patent No. 4,925,587	3.9	1.0	4.6	9.5

This example shows the performance characteristics of a preferred surfactant composition within the scope of the present invention. More specifically, the data presented above shows that the compound of Example 5 exhibits an unexpectedly high egg soil defoaming efficacy as defined by CSMA Method DCC-01, as well as a very low foam generating capacity as defined by Ross Miles Foam Height Test observed for this product type and

exc llent biodegradability as measured by standardized biodegradability test regimens OECD 301B and OECD 302A. The compound of Example 5 showed greater than 90% mineralization within 28 days using activated sludge in a modified Sturm Test. In addition, testing of this compound in a semi-continuous activated sludge (SCAS) test showed greater than 95% removal of the test compound over the five day test period, an excellent result. In addition, this product possesses excellent rinse properties as defined by CSMA Method DCC-05A, Glassware Deposition Rinse Test. This combination of properties make it ideal for use as an automatic dishwashing detergent/rinse aid.

EXAMPLE 6

Preparation of a Surfactant Composition Having a Poly(Ethylene Oxide) Backbone and Free of Poly(Propylene Oxide)

To a 2000 ml 3 necked round bottomed flask fitted with a thermometer (with a Thermo-Watch temperature controller), a magnetic stirrer, a 250 ml equilibrated dropping funnel (fitted with a nitrogen inlet), a nitrogen outlet, and a dry ice/acetone condenser was added 100 grams (0.694 moles) of Alfol-610 alcohol (Vista Chemical) and 0.4 grams of KOH. The alcohol was stirred at 120°C for 1½ hours. Ethylene oxide (610.1 grams: 13.88 moles) was then added under slow reflux over a period of 6-8 hours. The material was then post reacted for 3 hours. The dry ice/acetone condenser was then removed and 0.3 grams of KOHn was added and the

material was heated with stirring for 1½ hours. Then 127.7 grams (0.694 moles) of 1,2-epoxydodecane (AtoChem) was added dropwise over a period of 45 minutes at 120°C. The product was then brought to 150±3°C and post reacted for 4½ hours. The sample was cooled and removed from the flask. The product had a cloud point of 4°C, a hydroxyl number of 50.0 (MW=951), and was found to contain 14.4% primary hydroxyl.

EXAMPLE 7

Preparation of Another Surfactant Composition Having a Poly(Ethylene Oxide) Backbone and Free of Poly(Propylene Oxide)

To a 2000 ml 3 necked round bottomed flask fitted with a thermometer (with a Thermo-Watch temperature controller), a magnetic stirrer, a 250 ml equilibrated dropping funnel (fitted with a nitrogen inlet), a nitrogen outlet, and a dry ice/acetone condenser was added 100 grams (0.694 moles) of Alfol-610 alcohol (Vista Chemical) and 0.4 grams of KOH. The alcohol was stirred at 120°C for 1½ hours. Ethylene oxide (763.4 grams: 17.35 moles) was then added under slow reflux over a period of 6-8 hours. The material was then post reacted for 3 hours. 0.3 grams of KOHn was added and the material was heated with stirring for 1½ hours. Then 50.0 grams (0.694 moles) of 1,2-epoxybutane (Dow Chemical Co.) was added dropwise over a period of 1 hour at 120°C. The product was then brought to 150±3°C and post reacted for 4½ hours. The sample was cooled and removed from the flask. The product had a cloud

point of 88°C, a hydroxyl number of 45.9 (MW=1222), and was found to contain 22.8% primary hydroxyl.

EXAMPLE 8

Preparation of Another Surfactant Composition Having a Poly(Ethylene Oxide) Backbone and Free of Poly(Propylene Oxide)

To a 2000 ml 3 necked round bottomed flask fitted with a thermometer (with a Thermo-Watch temperature controller), a magnetic stirrer, a 250 ml equilibrated dropping funnel (fitted with a nitrogen inlet), a nitrogen outlet, and a dry ice/acetone condenser was added 100 grams (0.694 moles) of Alfol-610 alcohol (Vista Chemical) and 0.4 grams of KOH. The alcohol was stirred at 120°C for 1½ hours. Ethylene oxide (610.1 grams: 13.88 moles) was then added under slow reflux over a period of 6-8 hours. The material was then post reacted for 3 hours. The dry ice/acetone condenser was then removed and 0.3 grams of KOH was added and the material was heated with stirring for 1½ hours. Then 108.3 grams (0.694 moles) of 1,2-epoxydecane (AtoChem) was added dropwise over a period of 45 minutes at 120°C. The product was then brought to 150±3°C and post reacted for 4½ hours. The sample was cooled and removed from the flask. The product had a cloud point of 9°C, a hydroxyl number of 53.0 (MW=1058), and was found to contain 20.3% primary hydroxyl.

While the invention has been described above with reference to specific embodiments thereof, it is apparent that many changes, modifications and

variations can be made without departing from the inventive concept disclosed herein. Accordingly, it is intended to embrace all such changes, modifications and variations that fall within the spirit and broad scope of the appended claims.

WHAT IS CLAIMED IS:

1. A surfactant composition characterized by:
(a) a carrier selected from the group consisting of water, organic solvents, and combinations thereof, the total amount of said carrier being between about 0.01% and about 30% by weight based upon the weight of the composition; and
(b) an epoxy-capped poly(oxyalkylated) alcohol represented by the formula:
$R^3O[CH_2CH(CH_3)O]_x(CH_2CHR^4O)_y[CH_2CH(OH)R^5]_z$
wherein R^3 is a linear, aliphatic hydrocarbon radical having an average of from about 4 to about 18 carbon atoms including mixtures thereof; R^4 is hydrogen or a lower alkyl having between 1 and 6 carbon atoms; and R^5 is a linear, aliphatic hydrocarbon radical having an average of from about 2 to about 14 carbon atoms including mixtures thereof; x is zero or an integer having a value from 1 to about 5; y is an integer having a value from 1 to about 30; and z is an integer having a value of from 1 to about 3.

2. The surfactant composition of claim 1 characterized in that R^3 is selected from the group consisting of butyl, hexyl, octyl, decyl, and combinations thereof.

3. The surfactant composition of claim 1 characterized in that x has a value between 1 and 3, y has a value between 9 and 11, z has a value of 1, R^4 is hydrogen, and R^5 is a linear, aliphatic hydrocarbon radical having the structural formula $-(CH2)_3CH_3$

4. A surfactant composition comprising a liquid blend of components (a) and (b), each of said components being epoxy-capped poly(oxyalkylated) alcohols represented by the formulae:

(a) $R^1O[CH_2CH(CH_3)O]_p(CH_2CH_2O)_q[CH_2CH(OH)R^2]_r$ wherein R^1 is a linear, aliphatic hydrocarbon radical having an average of from 4 to 12 carbon atoms including mixtures thereof; and R^2 is a linear, aliphatic hydrocarbon radical having an average of from about 2 to about 4 carbon atoms including mixtures thereof; p is an integer having a value from 1 to about 5; q is an integer having a value from 1 to about 30; and r is an integer having a value of from 1 to about 3; and,

(b) $R^3O[CH_2CH(CH_3)O]_x(CH_2CH_2O)_y[CH_2CH(OH)R^4]_z$ wherein R^3 is a linear, aliphatic hydrocarbon radical having an average of from about 4 to about 18 carbon atoms including mixtures thereof; and R^4 is a linear, aliphatic hydrocarbon radical having an average of from about 2 to about 14 carbon atoms including mixtures thereof; x is an integer having a value from 1 to about 5; y is an integer having

a value from 1 to about 30; and z is an integer having a value of from 1 to about 3,

the weight ratio of component (a) to component (b) being within the range of between about 1:10 and about 10:1, with the proviso that amount of component (a) is sufficient to maintain said blend as a liquid.

5. The blend of epoxy-capped poly(oxyalkylated) alcohols of claim 4 characterized in that the weight ratio of component (a) to component (b) is between about 1 to 5 and about 5 to 1.

6. A liquid automatic dishwasher composition characterized by a blend of epoxy-capped poly(oxyalkylated) alcohols represented by the formula:

(a) $R^1O[CH_2CH(CH_3)O]_p(CH_2CH_2O)_q[CH_2CH(OH)R^2]_r$ wherein R^1 is a linear, aliphatic hydrocarbon radical having an average of from 4 to 12 carbon atoms including mixtures thereof; and R^2 is a linear, aliphatic hydrocarbon radical having an average of from about 2 to about 4 carbon atoms including mixtures thereof; p is an integer having a value from 1 to about 5; q is an integer having a value from 1 to about 30; and r is an integer having a value of from 1 to about 3;

(b) $R^3O[CH_2CH(CH_3)O]_x(CH_2CH_2O)_y[CH_2CH(OH)R^4]_z$ wherein R^3 is a linear, aliphatic hydrocarbon radical having an average of from about 4 to

about 18 carbon atoms including mixtures thereof; and R^4 is a linear, aliphatic hydrocarbon radical having an average of from about 2 to about 14 carbon atoms including mixtures thereof; x is an integer having a value from 1 to about 5; y is an integer having a value from 1 to about 30; and z is an integer having a value of from 1 to about 3; and,

(c) at least one component selected from the group consisting of detergent builder, bleach, anti-wear agent, and mixtures thereof,

the weight ratio of component (a) to component (b) being within the range of between about 1:10 and about 10:1, with the proviso that amount of component (a) is sufficient to maintain said blend as a liquid.

7. A liquid cleaning composition for cleaning hard surfaces characterized by containing an aqueous or organic solvent and a blend of epoxy-capped poly(oxyalkylated) alcohol surfactants represented by the formula:

(a) $R^1O[CH_2CH(CH_3)O]_p(CH_2CH_2O)_q[CH_2CH(OH)R^2]_r$

wherein R^1 is a linear, aliphatic hydrocarbon radical having an average of from 4 to 12 carbon atoms including mixtures thereof; and R^2 is a linear, aliphatic hydrocarbon radical having an average of from about 2 to about 4 carbon atoms including mixtures thereof; p is an integer having a value from 1 to about 5; q is an integer having a value from 1 to

about 30; and r is an integer having a value of from 1 to about 3; and,

(b) $R^3O[CH_2CH(CH_3)O]_x(CH_2CH_2O)_y[CH_2CH(OH)R^4]_z$ wherein R^3 is a linear, aliphatic hydrocarbon radical having an average of from about 4 to about 18 carbon atoms including mixtures thereof; and R^4 is a linear, aliphatic hydrocarbon radical having an average of from about 2 to about 14 carbon atoms including mixtures thereof; x is an integer having a value from 1 to about 5; y is an integer having a value from 1 to about 30; and z is an integer having a value of from 1 to about 3;

the weight ratio of component (a) to component (b) being within the range of between about 1:10 and about 10:1, with the proviso that amount of component (a) is sufficient to maintain said blend as a liquid.

8. A method for cleaning soiled tableware which is characterized by contacting the soiled tableware in a dishwashing machine in an aqueous wash bath having dispersed therein an effective amount of the composition of claim 1 to obtain clean tableware having substantially reduced films and spots.

9. A method for cleaning hard surfaces which is characterized by contacting the hard surfaces with an effective amount of the composition of claim 4 to obtain said cleaning of said hard surfaces.

10. A surfactant composition characterized by containing a liquid or solid carrier and a compound of the formula:

$R^6O[CH_2CH(CH_3)O]_d(CH_2CH_2O)_e[CH_2CH(OH)(CH_2)_3CH_3]_f$

wherein R^6 is a moiety selected from the group consisting of butyl, hexyl, octyl and decyl, and combinations thereof, d is an integer between 1 and 3, e integer between 9 and 11, and f is an integer between 1 and 3.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/12286

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :C11D 1/72, 3/075; C07C 41/01
US CL :252/174.22, 174.21, 174.19; 568/625, 622, 618, 606
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 252/174.22, 174.21, 174.19; 568/625, 622, 618, 606

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAS ONLINE: structures of epoxy-capped poly(oxyalkylated) alcohol

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,994,626 (GREENOUGH ET AL) 19 February 1991, abstract.	1-10
Y	US, A, 5,294,365 (WELCH ET AL) 15 March 1994, col. 1, lines 14-18.	1-10
A	US, A, 4,762,637 (ARONSON ET AL) 9 August 1988, col. 6, line 11 to col. 7, line 30.	1-10
A	US, A, 4,863,632 (ARONSON ET AL) 5 September 1989, col. 6, line 10 to col. 7, line 28.	1-10
A	US, A, 4,898,621 (PRUEHS ET AL) 6 February 1990, abstract.	1-10
A	US, A, 5,281,351 (ROMEO ET AL) 25 January 1994, col. 4, line 30 to col. 6, line 8.	1-10

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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INTERNATIONAL SEARCH REPORT

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PCT/US95/12286

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,925,587 (SCHENKER ET AL) 15 May 1990, abstract.	1-10
A	US, A, 4,317,940 (SCARDERA ET AL) 2 March 1982, abstract.	1-10
A	US, A, 4,207,421 (SCARDERA ET AL) 10 June 1980, abstract.	1-10
A	US, A, 3,956,401 (SCARDERA ET AL) 11 May 1976, abstract.	1-10
A	US, A, 4,827,028 (SCARDERA ET AL) 2 May 1989, col. 2, line 28 to col. 8, line 10.	1-10

Form PCT/ISA/210 (continuation of second sheet)(July 1992)*